4|PARTS

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Method of Forming Non-sag Molybdenum-Lanthana Alloys

5   TECHNICAL FIELD

This invention relates generally to methods for forming
dispersion-strengthened alloys of molybdenum. More
particularly, this invention relates to methods of forming
molybdenum-lanthana alloys having non-sag microstructures.

10

BACKGROUND OF THE INVENTION

Molybdenum alloys which have been dispersion-strengthened with
particles of lanthanum oxide (lanthana), La_2O_3, are desirable for
use in high temperature applications because of their high

15 melting point and good mechanical properties at high
temperatures, in particular, resistance to sag and creep. The
alloys are formed by combining molybdenum powder with from about
0.1 to about 5 weight percent (wt.%) of lanthanum oxide powder
or an equivalent amount of a lanthanum oxide precursor, such as

20 $La(OH)_3$ or $La(NO_3)_3$, which is then converted to the oxide by
heating. The size of the lanthanum oxide particles dispersed in
the molybdenum matrix is generally preferred to be less than
about 1 μm, however, the particles may be as large 5-10 μm.
After compacting and sintering, the sintered body is deformed by

25 mechanical working, e.g., rolling, swaging, drawing, or
hammering, and then is then recrystallized to generate the
desired microstructure. For sag and creep resistance, the
preferred microstructure consists of large, interlocking grains
which are elongated in the direction of the applied mechanical

30 work.

The recrystallization behavior of the alloy is affected by the
prior amount of deformation. When the undeformed or fully
recrystallized alloy is being cold worked, the density of
dislocations within the alloy increases. This occurs first at
the grain boundaries and then progresses further into the bulk
of the grains as the amount of cold work increases. Prior art
methods have employed high degrees of deformation (>60%) in
order to achieve high-temperature strength and creep-resistance.

Japanese Patent Publication 59-177345 (1984) describes a
molybdenum-lanthana alloy for structural purposes. The alloy
has a high secondary recrystallization temperature and high
high-temperature strength. The alloy contains 1 to 5 wt.%
lanthana (La_2O_3) particles having an average size of not more
than 3 μm which are uniformly dispersed in molybdenum. For
structural purposes, the material is preferably worked from the
sinter by a working factor of at least 60% and then heated above
the secondary recrystallization temperature.

U.S. Patent No. 4,950,327 to Eck et al. (1990) describes a high-
temperature, creep-resistant molybdenum-lanthana alloy having a
tiered structural arrangement. After sintering, the alloy is
mechanically reformed in gradations of about 10% without heating
the alloy above its recrystallization temperature. Once the
degree of reforming is at least 85%, the alloy is finally
subjected to a recrystallization anneal.

One disadvantage with the prior art methods is that the
dimensions of the feed material must be substantially greater
than the dimensions of the finally recrystallized material in
order to impart the required high degree of deformation. This

leads to less flexibility in the manufacturing process. Another
disadvantage is that the large amount of stored energy in the
material caused by the high degree of deformation can lead to
spontaneous grain growth in the material during
recrystallization. This may make it more difficult to control
grain size in the finally recrystallized material.

SUMMARY OF THE INVENTION

It has been discovered that a non-sag microstructure can be
obtained in a molybdenum-lanthana alloy using a degree of
deformation of from about 7% to about 18%. As used herein, the
degree of deformation refers to the percentage reduction in at
least one dimension of the feed material, e.g., sheet thickness.
Preferably, the degree of deformation is from about 12% to about
17%. The alloy may be deformed directly from the as-sintered
state to its finished form and then finally recrystallized or,
preferably, the alloy can worked from the as-sintered state to a
near-finished form, recrystallized, and then deformed to its
finished form and finally recrystallized. Preferably, the
recrystallization of the alloy in its near-finished form is
conducted at a temperature of from about 1150°C to about 1400°C.
The final recrystallization is preferably conducted at about
1900°C. Preferably, the amount of lanthana in the alloy ranges
from 0.4 wt.% to about 1.0 wt.%, more preferably, from about 0.6
wt.% to about 0.7 wt.%.

The grain size after final recrystallization is larger because
the predominant mechanism occurring during the heat treatment is
the annihilation of dislocations at the neighboring grain
boundaries causing some grain boundaries to disappear. This is
generally referred to as strain-induced grain boundary
migration. After final recrystallization, the grains tend to

- 3 -

exhibit less elongation than grains resulting from methods which use high degrees of deformation. Typically, the aspect ratio for the grains produced by the method of this invention is no more than 4:1. Also, since the degree of reformation needed to produce the non-sag microstructure is about 18% or less, the feed material need not be much larger than the finished product and there is a greater potential to control grain size in the finished material because of the lower amount of stored energy in the material prior to final recrystallization. Hence, the method of this invention is more flexible for manufacturers of refractory metal products.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1A is a photomicrograph of the microstructure of the molybdenum-lanthana alloy of Example 1 after recrystallization and rolling to 0.15 cm thickness.

Fig. 1B is a photomicrograph of non-sag microstructure of the molybdenum-lanthana alloy of Example 1 after final recrystallization.

Fig. 2A is a photomicrograph of the microstructure of the molybdenum-lanthana alloy of Example 2 after recrystallization and rolling to 0.10 cm thickness.

Fig. 2B is a photomicrograph of non-sag microstructure of the molybdenum-lanthana alloy of Example 2 after final recrystallization.

DETAILED DESCRIPTION OF THE INVENTION

For a better understanding of the present invention, together with other and further objects, advantages and capabilities

- 4 -

thereof, reference is made to the following disclosure and
appended claims taken in conjunction with the above-described
drawings.

EXAMPLE 1

Pure molybdenum metal powder with grain size of 3.5 μm was mixed
with 0.7 weight percent (wt.%) of La(OH)₃ powder having a grain
size of 0.65 μm. The mixture was isostatically pressed at 240
MPa to form a pressed slab with dimensions of 64 cm x 38 cm x 5
cm. The slab was subsequently rolled at varying temperatures;
starting at 980°C, followed by 785°C, and finally at ambient
temperature to a thickness of 0.17 cm. The sheet was then
recrystallized at 1400°C and then rolled at ambient temperature
to the thickness of 0.15 cm, (about 12% deformation). The
microstructure of the recrystallized and rolled sheet is shown
in Fig. 1A. The rolled sheet was subjected to a final
recrystallization anneal at 1900°C to produce the non-sag
microstructure which is shown in Fig. 1B.

Example 2

Pure molybdenum metal powder with grain size of 3.5 μm was mixed
with 0.7 wt.% La(OH)₃ powder with a grain size of 0.65 μm. The
mixture was isostatically pressed at 240 MPa to form a pressed
slab with dimensions of 64 cm x 38 cm x 5 cm. The slab was
subsequently rolled at varying temperatures; starting at 980°C,
followed by 785°C, and finally at ambient temperature to a
thickness of 0.12 cm. The sheet was then recrystallized at
1150°C. Subsequently it was rolled at ambient temperature to the

thickness of 0.10 cm (about 17% deformation). The
microstructure of the recrystallized and rolled sheet is shown
in Fig. 2A. Upon a final recrystallization anneal at 1900°C, the
sheet material exhibited the non-sag microstructure shown in
Fig. 2B.

The sag resistance of 0.5 in. x 5.6 in. samples of the non-sag
molybdenum-lanthana sheet material from Examples 1 and 2 was
measured according to the following procedure. The samples were
supported at opposite ends and a 10 g weight placed on the
sample at the center point between the supports. The distance
between the supports was 4.2 inches. At the start of the test,
the distance between the reference plate and the 0.15-cm-thick
sample was 0.5 in. at the point directly below the 10-g load.
The corresponding distance for the 0.10-cm-thick sample was
0.4375 in. at the start of the test. Sag was measured as the
amount of deflection of the sample toward the reference plate
after heating the sample at 1900°C for 1 hour. Six such heating
cycles were carried out for each sample and the amount of
deflection measured after each cycle. The cumulative amount of
deflection is reported in the following table. The sag
resistance of the materials was found to be equivalent to
commercially available non-sag molybdenum-lanthana sheet
material.

Table

Material Thickness	Width (in.)	Length (in.)	Center Load (g)	Total Sag (in.)
0.15 cm	0.5	5.6	9.99	0.0625
0.10 cm	0.5	5.6	9.98	0.0313

While there has been shown and described what are at the present
considered the preferred embodiments of the invention, it will
be obvious to those skilled in the art that various changes and
modifications may be made therein without departing from the
scope of the invention as defined by the appended claims.